RI 9453

REPORT OF INVESTIGATIONS/1993

Rare-Earth Occurrences in the Pea Ridge Tailings

By C. W. Vierrether and W. L. Cornell

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

at. pct	atomic percent	min	minute
cm	centimeter	μm	micrometer
ft	foot	mt	metric ton
g	gram	pct	percent
lb/mt	pound per metric ton	wt pct	weight percent

RARE-EARTH OCCURRENCES IN THE PEA RIDGE TAILINGS

By C. W. Vierrether[1] and W. L. Cornell[2]

ABSTRACT

Tailings from the Pea Ridge iron mine contain significant amounts of apatite, which has rare-earth element values associated with it. In association with the recovery of rare-earth minerals as a secondary resource, the U.S. Bureau of Mines conducted an investigation on the recoverability of the rare-earth minerals from these tailings. The mill tailings were subjected to a phosphate flotation to separate the apatite from other constituents. More than 70-pct recovery of the rare-earth values was achieved. Based on mineralogical characterization and prior analysis of rare-earth-bearing breccia pipe material at Pea Ridge, it is proposed that processing this phosphate concentrate on a vanner table would yield up to a 95-pct recovery of the rare earths in the concentrate, with the apatite reporting to the tailings.

Intensive ore microscopy studies of the original tailings to the flotation products led to the identification of monazite, xenotime, and rare-earth-enriched apatite as the major rare-earth-bearing minerals in the tailings.

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INTRODUCTION

The ore body at Missouri's Pea Ridge Iron Ore Co. is classified as a magnetite Fe deposit that contains apatite (*1*).[3] Ore of this type is also encountered at deposits such as Mineville, NY, and Kiruna, Sweden (*1-2*). Apatite in the Pea Ridge magnetite ore contains rare-earth elements (REE) in significant concentrations. Apatite from Mineville contains an average of 11.14 pct total rare-earth oxides (REO) (*3*). Apatite in grab samples from Pea Ridge contains as much as 0.72 pct REO with the average being 0.52 pct. Phosphorous concentrations at Pea Ridge generally decrease with depth, except for a concentration spike at the 1,975-ft level (table 1) (*4*). Apatite is the main P-bearing mineral at Pea Ridge (*1*).

Table 1.—Phosphate concentrations with depth

Mine level, ft	*Phosphorous, wt pct*
1,675	1.42
1,825	.74
1,975	1.08
2,175	.66
2,275	.41

Apatite is described by John Emery (*1*) as occurring "as inclusions in the magnetite in veins, and as crystals in vugs. Invariably, it is coarser grained than the magnetite and occasionally forms large crystals in incipient vein-like structures. Apatite appears to be consistent in quantity throughout the deposit." Apatite contributes P to the Fe pellets, which in turn causes the steel to be brittle. Therefore, the apatite is removed from the magnetite ore by flotation. In the early history of the mine, the apatite concentrate from flotation was sold as a fertilizer; now it is mixed with the hematite tailings from magnetic separation and pumped to tailings ponds. In the absence of an apatite circuit, Pea Ridge tailings produced each year contain 1,000 mt REO.

REE are contained in the apatite $[Ca_5(PO_4)_3(F,Cl,OH)]$ (*5*) as substitutions for Ca^{2+} and as inclusions of REE-bearing minerals (fig. 1). These REE-bearing mineral inclusions are probably oriented parallel to the c-axis of the apatite, which is similar to inclusions in apatite described elsewhere (*6*). The major REE-bearing minerals identified were monazite $[(Ce,La,Y,Th)PO_4)]$ and xenotime (YPO_4). X-ray energy dispersive X-ray (EDS) data indicate there are several minor REE-bearing minerals in the tailing. Characterization of these minor minerals and a more detailed examination of the monazite and xenotime are currently in progress at the U.S. Bureau of Mines.

Prior beneficiation test work on the rare-earth-bearing breccia pipes has resulted in REE concentrates of 62 pct total REO with a 95-pct recovery (*7*). The tailings from Pea Ridge were subjected to this same regimen of bench work. These preliminary bench-scale separation tests and characterization study will be used to determine the feasibility of recovering the REE from the mine tailings.

This work was done in support of the Bureau's goal to help ensure a domestic supply of minerals and materials.

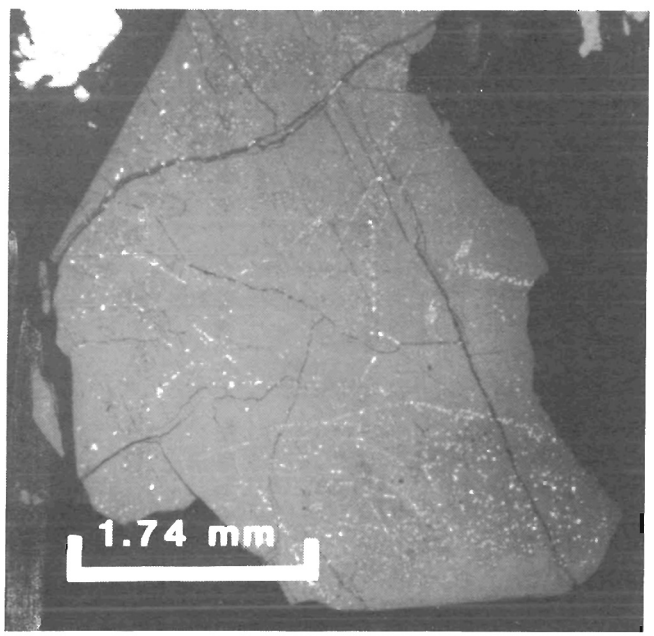

Figure 1.—SEM backscattered micrograph of apatite crystal with rare-earth inclusions parallel to c-axis.

[3]Italic numbers in parentheses refer to items in the list of references at the end of this report.

INSTRUMENTATION

Examinations were conducted on two instruments to provide accurate mineral identifications. Reflected light microscopy was performed on a Zeiss[4] Universal R microscope to provide preliminary identification of apatite in the mounted ore, tailings, and flotation products.

More indepth examinations were performed with a scanning electron microscope (SEM) equipped with EDS. Analyses with the SEM and EDS were semiquantitative or standardless. Major elemental constituents identified by EDS in the apatite and other rare-earth-bearing minerals are Ca, P, Fe, Cl, Ce, La, and Y with traces of other REE. Oxygen, fluorine, and other light elements were not analyzed because of unavailability of equipment.

REE-BEARING MINERAL CHARACTERIZATION

Screen analysis was conducted on a sample from the commercial fertilizer phosphate circuit, which is currently inactive (table 2). The large percentage (more than 70 pct) of phosphate in the plus 37-μm fraction indicates that the majority of the apatite occurs in this fraction. A screen analysis of the as-is mill tailings showed that more than half of the Ce values were in the minus 37-μm fraction (table 3). This indicates that the majority of rare earths occur in this size fraction. The 7.33 pct phosphate in the plus 37-μm fraction indicates the majority of the apatite in the as-is mill tailings is larger than 37 μm.

SEM analyses showed that the average size of the rare-earth minerals included in the apatite was 10 μm. SEM analysis illustrated that the rare-earth concentration in the plus 37-μm fractions of both samples were due to rare-earth mineral inclusion in the apatite. These inclusions were identified as xenotime, monazite, britholite, and an unidentified silico monazite (*8*). Examination of the minus 37-μm fraction showed that the rare-earth minerals present occurred as liberated particles.

APATITE

The apatite commonly occurs as anhedral grains with some euhedral grains up to 0.5 cm in diameter and 1.5 cm in length. It is predominantly brown to reddish-brown and, in rare occurrences, green to colorless. The green color is attributed to Fe contamination in the apatite crystal structure. A reddish-brown apatite at Mineville was attributed to mineral inclusions and coatings of monazite and bastnaesite by McKeown and Klemic (*3*). The majority of apatite studied for this report was reddish-brown. Although there were inclusions of monazite and xenotime, there was no coating noticed in the ground samples and only one instance of a coating, by xenotime, in the bulk rock samples. Non-rare-earth-bearing mineral inclusions in the apatite include magnetite, rutile, pyrite, calcite, dolomite, and an Mg-Al spinel. In some areas of the mine, calcite appears to have replaced much of the apatite. In these areas, the abundance of apatite varies inversely with the calcite content (*1*).

Table 2.—Phosphate circuit size analysis

Size, μm	Wt pct	Grade, wt pct		
		Ce	La	Y
Plus 150	3.02	0.29	0.21	0.24
Minus 150 plus 100	8.21	.29	.19	.27
Minus 100 plus 74	16.93	.35	.15	.26
Minus 74 plus 44	36.58	.30	.18	.26
Minus 44 plus 37	6.02	.42	.27	.24
Minus 37	29.06	1.40	.92	.26
Total	[1]100.00	3.05	1.92	1.53

[1]Numbers do not add to total shown because of rounding.

[4]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

Table 3.—Pea Ridge tailings size analysis

Size, μm	Wt pct	Grade, wt pct				Recovery, wt pct			
		Ce	Y	Fe	PO_4	Ce	Y	Fe	PO_4
Plus 37	33.3	0.10	0.08	22.4	7.33	22	33	23	71
Minus 37	66.7	.18	.08	37.9	5.82	78	67	77	29
Calculated head	100.0	.15	.08	32.7	6.32	100	100	100	100

Pea Ridge apatite with REE-bearing mineral inclusions contains <1.20 pct of total REO substituted for Ca^{2+}. These REE are primarily Ce, Nd, La, Ho, Gd, Sm, Y, Dy, and Yb (table 4). The overall Th content in the Pea Ridge mill tailings is extremely low at <0.5 wt pct. Apatite exclusive of inclusions has no detectable REE. In the samples with apatite crystals, there was no REE-bearing apatite adjacent to non-REE-bearing apatite. REE-bearing mineral inclusions in apatite appear to be vertically zoned throughout the deposit, with plentiful inclusions at depth and inclusion-free apatite adjacent to interstitial discrete crystals of monazite at higher levels. These characteristics suggest that monazite and xenotime inclusions in apatite formed by exsolution from hydrothermal fluids as temperature decreased. Åmli (*6*) and McKeown and Klemic (*3*) reported similar inclusions in apatite in the Gloserheia granite pegmatite, Norway, and in the Mineville district, NY, respectively.

Table 4.—Rare-earth element substitution in Pea Ridge apatite

Element	R_2O_3, *wt pct*
Ce	0.34
Nd	.32
La	.25
Ho	17
Gd	.16
Sm	.12
Y	T
Dy	T
Yb	T

T Trace.

Although there is no zoning of the REE in the apatite, there is distinct zoning of chloride concentrations in the apatite (fig. 2). The chloride-enriched zone is in the outer portions of the apatite crystals. The interesting aspect noted with this zoning is the depletion of REE-bearing mineral inclusions in the chloride zone. Chloride concentration varies from 3 to 5 wt pct. The boundaries between the phases are sharp and distinct, rather than gradational.

XENOTIME

Xenotime in the tailings is smaller in size and substantially less abundant than that in the breccia pipe material (*9*). The xenotime particles examined ranged in size from 15 μm to <10 μm with the majority being 12 μm. Xenotime inclusions in apatite are always adjacent to monazite inclusions (fig. 3).

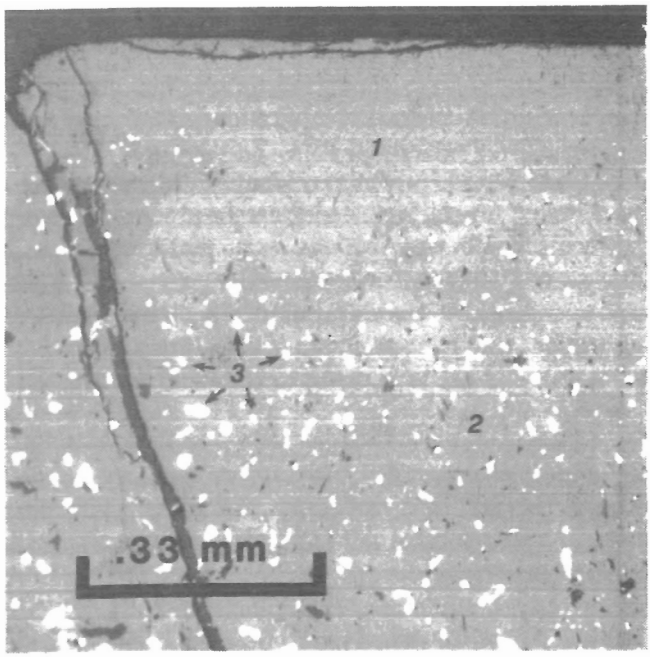

Figure 2.—SEM backscattered micrograph of (1) high chloride zone, (2) low chloride zone in apatite, and (3) rare-earth inclusions.

The composition of the xenotime, as illustrated in figure 4, is toward the lower range of accepted xenotime values (*10*). The method for reporting elemental distribution of REE by comparing them with relative rare-earth concentrations in Bronzite Chondritic meteorites has been adopted (*10*). The composition of xenotime does not appear to be homogeneous throughout each crystal. Figure 5 indicates the partial zoning or banding that was observed in the xenotime particles examined for this report. Åmli (*6*) reported that xenotime in the Gloserhiea Granite pegmatites is zoned from the center to the rim. Concentric zoning in the xenotime from Pea Ridge can be divided into three separate zones (see table 5). Variations in REE concentrations were used to define these zones. The inner zone has higher concentrations of Y, Ce, La, and Nd with respect to the middle and outer zones. The middle zone is defined by having the lowest Y concentration and the highest Yb concentration. The outer zone has the lowest Ce, La, and Nd concentrations and the highest Dy, Gd, and Th concentrations. These elemental values are average values from energy dispersive pseudo line scans of 10 xenotime particles. The xenotime associated with the apatite in the magnetite ore body compositionally resembles the xenotime in the breccia pipes (*9*). This suggests a similar source for the deposition of xenotime in both occurrences.

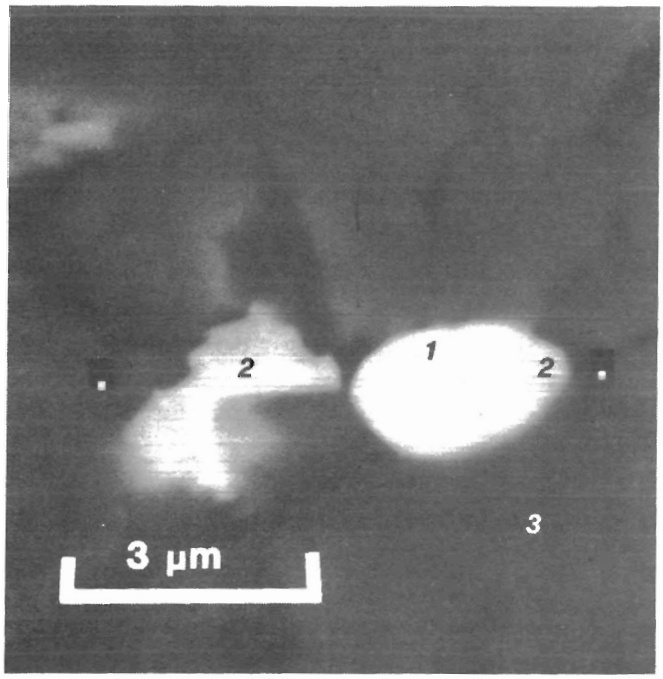

Figure 3.—SEM backscattered micrograph of (1) monazite particle adjacent to zoned (2) xenotime in (3) apatite.

Table 5.—Elemental zoning of R_2O_3 in Pea Ridge xenotime, weight percent

Element	Outer zone	Middle zone	Inner zone
Y	57	55	59.5
P_2O_5	29.2	29.1	29.3
Ce	ND	ND	5.9
La	ND	ND	3.5
Nd	ND	ND	.6
Dy	3.4	1.1	.6
Yb	2.3	2.8	.6
Gd	1.7	1.1	.6
Th	1.1	T	ND

ND Not detected.
T Trace.

MONAZITE

Anhedral monazite occurs as both liberated and unliberated particles from 50 to 10 μm in size (fig. 6). Microscopic examination of the plus 37-μm fraction showed the monazite to be unliberated. Examinations of the minus 37-μm fraction yielded the opposite: Most of the monazite was liberated. The elemental composition of the monazite in the tailings is in the middle of the accepted range for monazite (table 6) (*10*) (fig. 7). Monazite

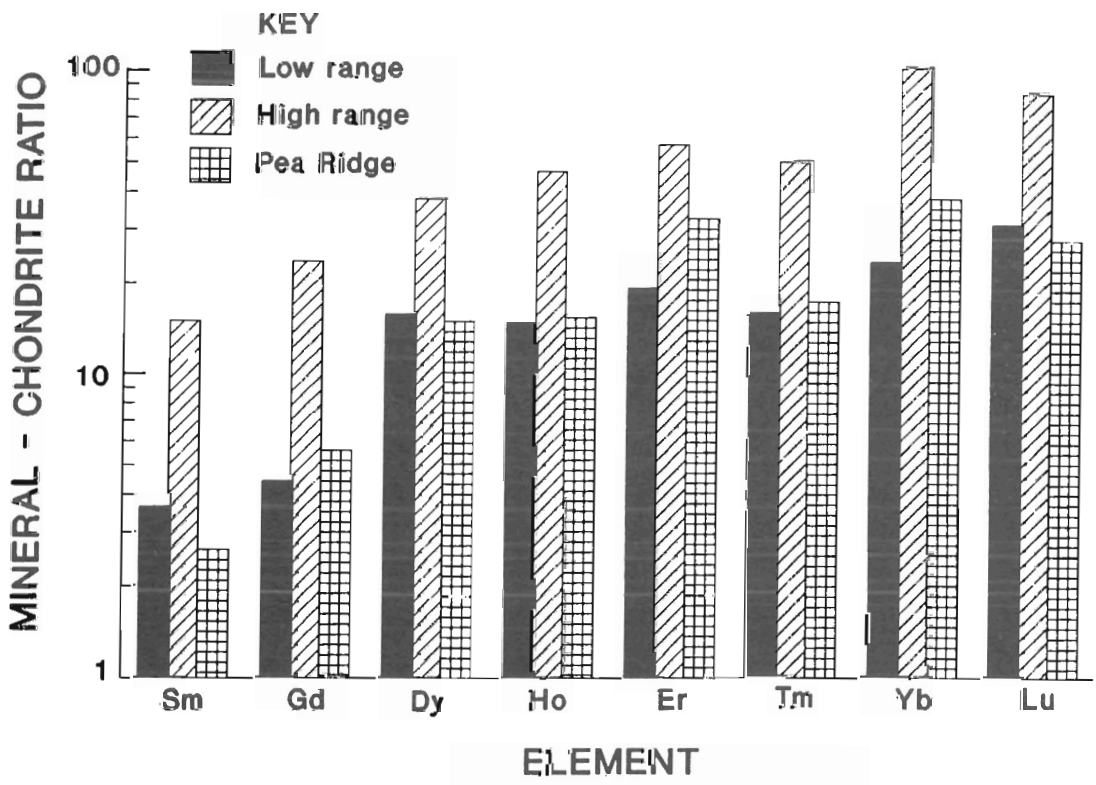

Figure 4.—Pea Ridge xenotime compared with high and low elemental concentrations. Mineral-chondrite ratio uses mean chondrite values (*8*).

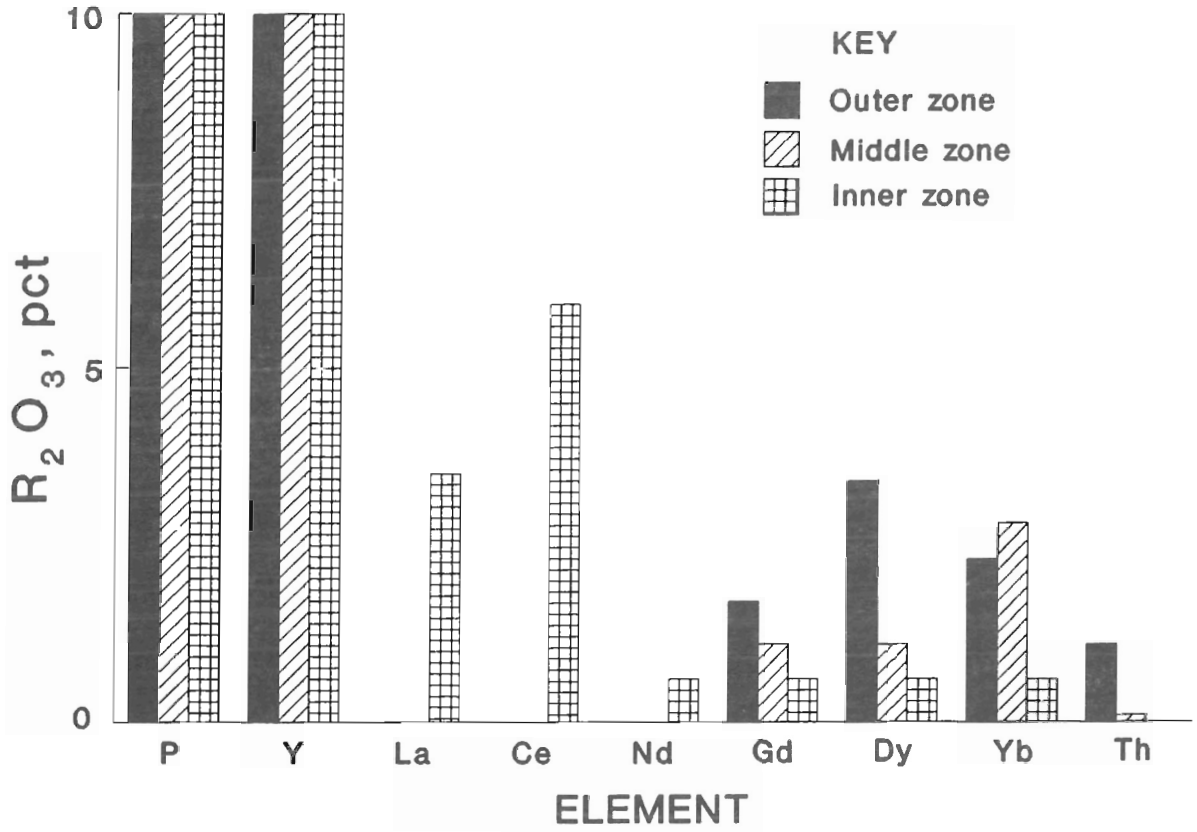

Figure 5.—Elemental zoning in xenotime.

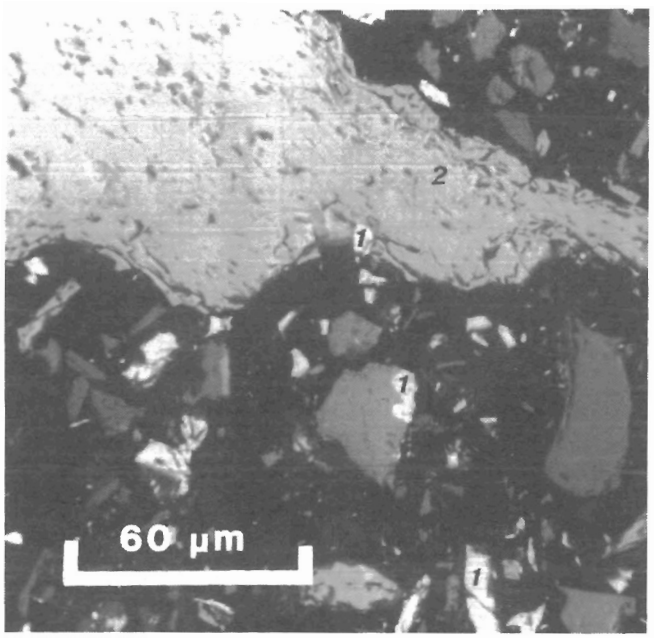

Figure 6.—SEM backscattered micrograph of (1) monazite as liberated and unliberated phases in (2) apatite in unscreened Pea Ridge tailings.

particles were also observed included in magnetite, and in one instance, magnetite rimmed a monazite inclusion on the edge of an apatite particle. Also observed with monazite inclusions was an Mg-Al spinel. Monazite was observed adjacent to rutile in two apatite particles. The monazite, unlike xenotime, is homogenous and exhibits no elemental zoning. In both the monazite and xenotime, the Th concentration is low, <2.0 pct REO. Beach sands commonly have up to 12 pct REO, causing a disposal problem because of the radioactive decay of Th (*11*).

Table 6.—Composition of Pea Ridge monazite

Element	*R_2O_3, wt pct*
Ce	34.6
La	28.9
P_2O_5	18.0
Nd	11.9
Pr	4.0
Sm	2.2
Gd	1.1
Eu	T

T Trace.

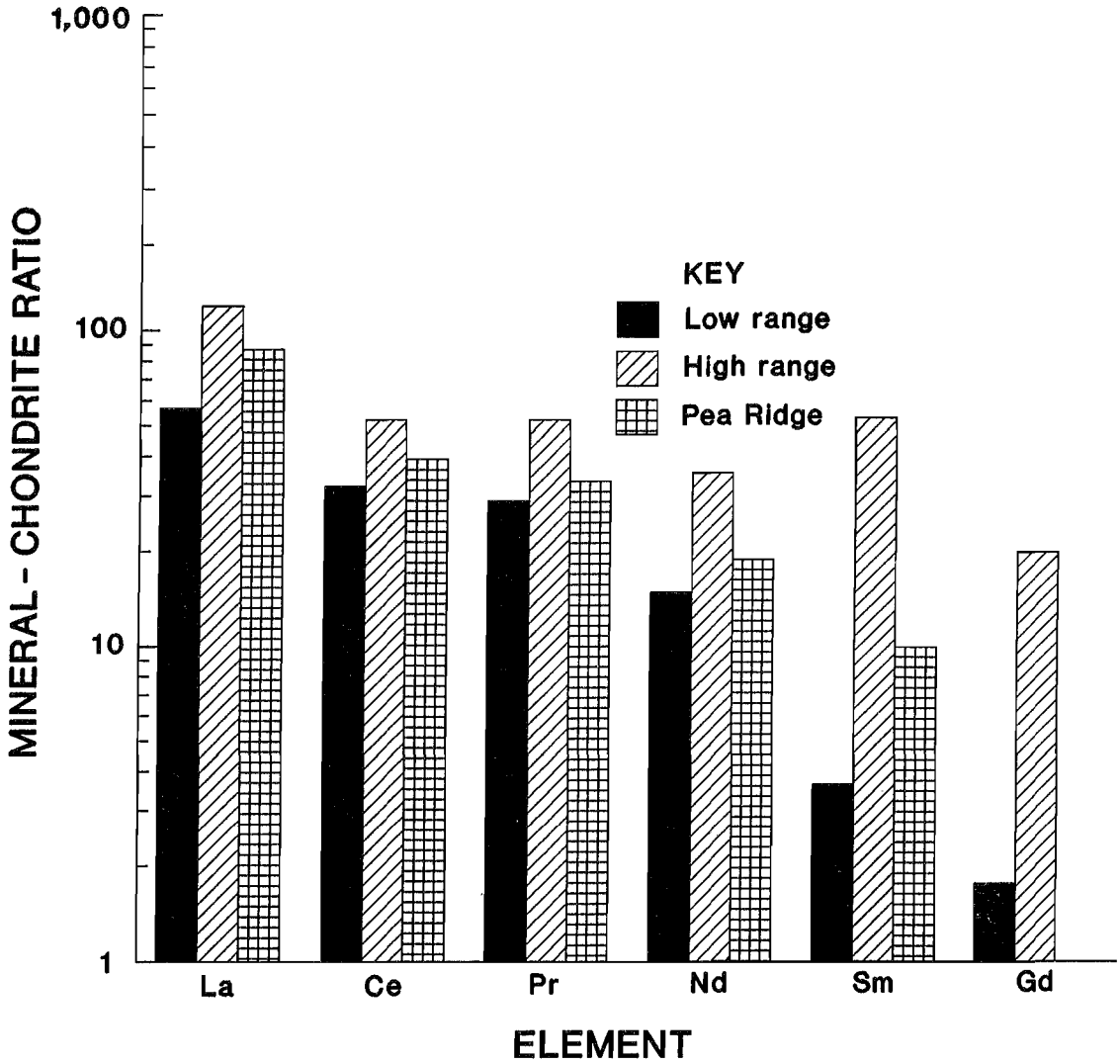

Figure 7.—Pea Ridge monazite compared with high and low elemental concentrations.

OTHER REE-BEARING MINERALS

Other possible REE-bearing minerals occur in the magnetite ore body associated with or included in the apatite. These minerals are a silico monazite that is possibly cheralite, britholite, and bastnaesite. The silico monazite-like phase could not correctly be determined with X-ray diffraction techniques because of its trace concentration. In order to be considered cheralite, a monazite phase should exhibit an atomic percent ratio of (Th + U + Ca) (Ce + La + Pr + Nd) equal to 1.47. The highest ratio of these elements measured by EDS in the silico-monazite phase was 1.0, and the lowest was 0.02. These results excluded cheralite from further consideration (*12*) (fig. 8).

The silico monazite is considered a variety of monazite based on the Σ(La + Ce + Pr) atomic percent. Values reported in the literature range from 66.2 pct at Mountain Pass, CA, to 42.9 pct for monazite-(Nd) (*2*). Monazite from Mountain Pass approaches the theoretical value of 69.7 pct, Ce-La = 1:1, because it has low Ca and Th substitutions for Ce in the lattice structure. The lower value of 42.9 pct for monazite-(Nd) is attributed to anomalously high values of Nd and Sm. The Σ(La + Ce + Pr) for Pea Ridge monazite is approximately 50 at. pct, ±5 pct, with the silico monazite at 47 at. pct, ±5 pct, which is well within the range defined for monazite. The Nd and Sm concentrations are not anomalously high in the silico-monazite from Pea Ridge. The silico monazite could be an alteration of monazite. Depending upon the Th

concentration, the Si substitution for P could be to counterbalance the internal charge of the crystal because the Th concentration is elevated (*13*).

Britholite is related to apatite through the substitution of (Re^{3+} + Si^{4+}) for (Ca^{2+} + P^{5+}). It is a late-stage mineral in the apatite series depicted by the vector diagram in figure 9 (*14*). This makes it unclear as to whether britholite crystallizes directly from the rare-earth-enriched magma instead of apatite, or whether it is a postmagmatic recrystallization of the preexisting apatite (*15*). Bastnaesite was identified by SEM analyses based on the Ce-La ratio in the absence of P. Only two bastnaesite grains were observed; both were inclusions in the apatite that exhibited calcite alteration.

MINERAL PROCESSING

Economical recovery of REE from apatite has been well documented (*16*). Accepted industry practice has been to selectively acid leach the REE from the phosphate. This method is used on the Palaborwa carbonatite of South Africa where the apatite concentrate contains 0.6 to 0.85 wt pct REO (*17*). Even though this is the accepted method, REE recovery can also be accomplished using physical separation techniques. The following describes a method for accomplishing this recovery.

Approximately 700 g of the minus 37-μm tailings material was pulped to 12 pct solids by volume. The pulp was treated with 0.27 lb/mt oleic acid as a phosphate collector and 0.06 lb/mt pine oil as a frother. The pH was adjusted to 7 with H_2SO_4. Flotation proceeded for 4 min each in three successive steps with reagents added at each step. The concentrates were collected after each step to determine the amount of phosphate recovered in each step (table 7).

The flotation recovered more than 70 pct of the phosphates from the tailings, with more in the second step than in the first or third. The proposed next step is to combine the concentrates from the flotation and process

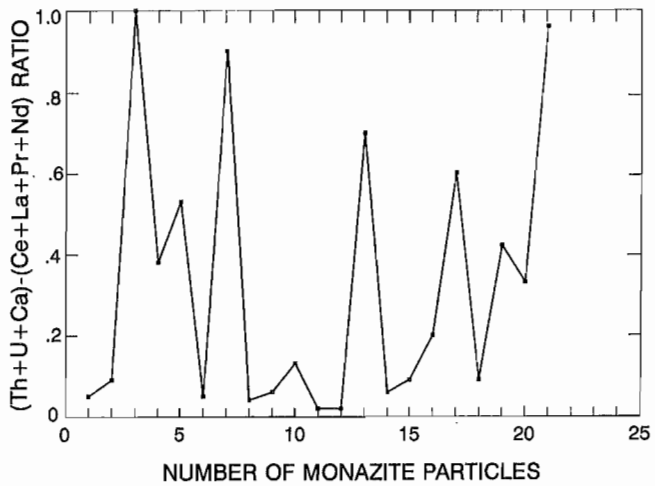

Figure 8.—Ratio of (Th + U + Ca) (Ce + La + Pr + Nd) in monazite particles.

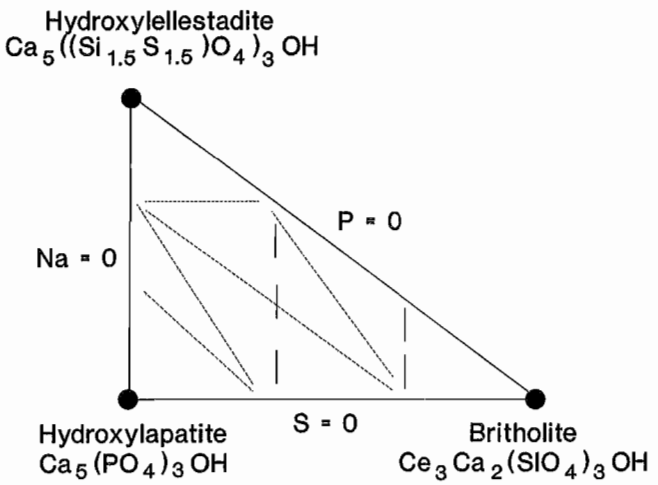

Figure 9.—Apatite vector diagram depicting relationship with britholite.

Table 7.—Pea Ridge tailings phosphate flotation

(All values are in weight percent)

Stream	Weight	RE_2O_3	Grade			Recovery		
			Ce	Y	PO_4	Ce	Y	PO_4
Concentrate:								
1	6.95	1.04	0.29	0.10	24	21	23	27
2	13.97	.85	.24	.08	18	35	37	41
3	7.97	.64	.18	.06	12	15	16	15
Tailings . . .	71.12	.14	.04	.01	6	29	23	17

them on the small Bartles-Mozley vanner table (fig. 10). The phosphate concentrate from the breccia pipes treated in this manner recovered up to 95 pct of the REE in the concentrate. Based on the microscopic examinations of the mill tailings, there is enough evidence to say that a phosphate concentrate from the tailings might respond in a similar manner to gravity separation as that of the breccia pipe material. Based on the apparent differences in the specific gravity of apatite, 3.2, and the rare-earth phosphates, 4.4 to 5.4, the apatite would be expected to report to the gravity tailings (*18*).

The apparent success of the recovery of the rare earths by these means is very attractive in that the tailings from the magnetite processing can be routed, after screening to minus 37 μm, to the circuit used to recover REE from the breccia material. The plus 37-μm fraction can be ground to minus 37 μm to liberate the remaining rare-earth minerals and then routed through the same circuit (fig. 10).

Added attractions to this proposed recovery of the REE from the tailings is the total amount of individual REE such as Nd, Sm, and Dy (see figures 4 and 7). Although these are not extraordinarily high, they are significant for this "ore body" (*19*).

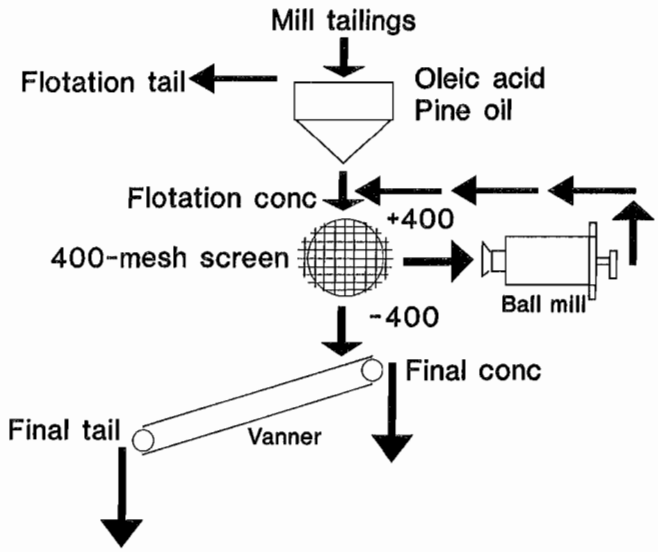

Figure 10.—Proposed Pea Ridge tailings circuit for recovery of rare-earth minerals.

CONCLUSIONS

REE are present in four identifiable minerals in the tailings at Pea Ridge. These are apatite, monazite, xenotime, and britholite. There is also an unidentified silicomonazite present with the apatite in the magnetite.

Promising initial separation tests, successful testing on the REE-bearing breccia pipes, and prior production of a phosphate concentrate support the idea that rare earths can be recovered from the magnetite ore. Significant REE concentrations of Nd, Sm, and Dy and the low Th concentration of the tailings are an added incentive to pursue mineral processing of the Pea Ridge mill tailings.

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